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# **SOLID-LIQUID EQUILIBRIA FOR THE DIMETHYL ETHER + CARBON DIOXIDE BINARY SYSTEM**

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## **Abstract**

A recently built experimental set-up was employed for the estimation of the solid-liquid equilibria of alternative refrigerants systems. The behavior of dimethyl ether + carbon dioxide was measured down to temperatures of 131.6 K.

To confirm the reliability of the apparatus, the triple point of the dimethyl ether was measured. The triple point data measured revealed a good consistency with the literature.

The results obtained for the mixtures were corrected by the Rossini method and interpreted by means of the Schröder equation.

## **Introduction**

The dimethyl ether (DME) + carbon dioxide (CO<sub>2</sub>) mixture can be an attractive option for different applications. In a recent paper, the present system was proposed as a solvent [1], and its solvent properties were characterized and relative permittivity at elevated pressures was measured. The Phase behavior of biodegradable polymers in dimethyl ether and dimethyl ether + carbon dioxide was also studied [2].

A very interesting application lies also on the refrigeration applications. In fact, this refrigerant mixture does not deplete the ozone layer, and has a low global warming potential. An US patent proposed this safe, non-toxic refrigerant mixture for heating/hot water supply which operates at low pressures while exhibiting excellent performance [3].

General interest on the thermophysical properties of DME fluid and its binary mixtures recently arised also from our research group [4-5].

When lower temperatures are needed in the refrigerating units, the lowest evaporator temperature achievable can be limited by the melting temperature of carbon dioxide ( $T_m = 216.58$  K). For this reason, in some applications the low temperatures can be achieved by using blends.

Data on solid-liquid equilibria (SLE) are important in refrigerating industry defining the lowest temperature limit at which the refrigerant may circulates in fluid state. In addition, SLE provide theoretical information on the behavior of studied systems at low temperatures in terms of activity coefficients. But, in a fact, the SLE for mixtures containing HFCs refrigerants are extremely scarce in literature.

Due to expected temperatures of the SLE of the refrigerant systems that usually spans from about 100 up to 217 K (in case of CO<sub>2</sub> as the mixtures component), SLE measurements generally creates difficulties in the visual observation of the disappearance of the last amount of solid phase. Hence a set-up was specifically built<sup>1</sup> avoiding the need of the visual observation of phase behavior.

Recently, our lab measured the SLE of several (CO<sub>2</sub> and N<sub>2</sub>O) + HFCs binary systems [6-10]. In this paper, the SLE for CO<sub>2</sub> + DME binary system was measured down to temperatures of 131.6 K.

## **Experimental Set-up and Procedure**

The apparatus comprises a measuring cell and a system for drawing the liquid nitrogen directly from its insulated tank with the aid of compressed air: the carrier fluid circulating in the circuit is thus the refrigerant fluid itself.

The experimental setup is shown in Figure 1. The measuring cell (1) was made out of a stainless steel cylinder with a cover welded to the body. The volume was of approximately 47 cm<sup>3</sup>. A stirrer (2) was placed in the cell. Two holes were drilled in the cover, and a stainless steel tube was inserted through and welded to the hole on the left for charging the cell with gas, while the hole on the right was used to house the thermometer (3). The purpose of the stirrer was to prevent any premature stratification of the fluids comprising the various mixtures, while also assuring greater homogeneity during the liquefaction and crystallization of the mixture. The stirrer inside the cell was turned by a magnet, which drives the plate welded onto the lower end of the rod. An absolute pressure transducer (HBM, Mod. P8A) (4) was installed in the charging tube. A mass flow control (5) was installed upstream from the dehumidifier: a needle valve with a shutter was used to adjust the flow rate coming from the dry air supplier (6), as measured by means of the pressure difference read on a pressure gauge alongside it. The airflow was also measured by a rotameter (7).

The operation of the system as a whole can be divided into two separate circuits and consequently two operating modes: a cooling and an heating mode.

*Cooling mode.* The cooling system as a whole is composed by four functional parts: the compressed air circuit that creates a positive pressure in the liquid nitrogen tank, the thermally-insulated liquid nitrogen tank (8), the hose connecting the tank to the circuit, complete with a faucet, and the copper coil that surrounds and exchanges heat with the cell.

The core element in the whole cooling system is the copper coil surrounding the measuring cell; through its contact surface, the coil removes heat by means of the refrigerant fluid flowing inside it. The copper coil and cell are placed together inside a Dewar flask (9) so as to further isolate them from the outside environment. The system as a whole is suitably covered with neoprene foam for thermal insulation.

When the system is used in the cooling mode, the compressed air (after passing through suitable dehumidifier filters) is delivered to the liquid nitrogen tank, which is thus placed under a positive pressure. Inside the tank, a PVC hose draws the refrigerant fluid from the bottom, which begins to

flow through the circuit as soon as the pressure in the tank, controlled by a manometer (10), is sufficient to overcome the load losses produced by the circuit. When a steady state is reached, the liquid nitrogen flows through the circuit, rapidly cooling all of its surfaces to a very low temperature. The refrigerant fluid passes first through the silicone capillary, then through the copper piping, exchanging heat with the measuring cell by evaporation as it moves through the coil, and finally flows out from the nitrogen outlet (11). In this cooling configuration, the nitrogen valve remains open and the heating circuit valve remains closed.

*Heating mode.* When the system is operated in the heating mode, the dehumidified compressed air circuit is connected directly to the measuring cell's circuit and, in this case, the air acts as a carrier fluid and warms the cell, which is at a very low temperature by the end of a measuring procedure. In this configuration, the nitrogen inlet valve remains closed. An external copper coil (12) has also been provided: this can be heated by the operator to speed up the warming of the measuring cell.

*Temperature Measuring System.* To monitor the temperatures, the apparatus was equipped with one thermoresistance put in the measuring cell. The system parameters and the efficiency of the coil immersed in the liquid nitrogen were assessed using thermocouples at specific points on the copper tube. The platinum resistance thermometer used in the apparatus (100  $\Omega$ , Minco, Mod. S7929) was calibrated by comparison with a 25  $\Omega$  platinum resistance thermometer (Hart Scientific, Mod. 5680 SN1083).

*Experimental Procedure.* The charging procedure consisted of the following steps: the bottle containing the refrigerant gas (13) was weighed on the electronic balance (the uncertainty of which is 0.5 mg); then the bottle was connected to the apparatus and to the vacuum pump (14) (Vacuubrand, Mod. RZ2), a vacuum was created inside the measuring cell and the charging tube as recorded on the vacuum pump gauge (Galileo, Mod. OG510); then the fluid was charged by opening the valve on the gas bottle; the temperature of the cell was brought down by a flow of liquid nitrogen so as to insert the whole mass in the cell, leaving as little as possible in the charging tube; a suitable time interval was allowed so that the pressure, being lowered by the temperature

reduction, could drop to below atmospheric pressure, then the on/off valve was closed; and the gas bottle was disconnected and weighed again to establish the actual mass charged in the cell.

The coil with liquid nitrogen was wrapped around the measuring cell. Monitoring the time dependence of temperature, a cooling curve was obtained for each sample concentration. While the change of phase occurs, the heat removed by cooling is compensated for by the latent heat of the phase change, showing a change of slope in the temperature trend. The arrest in cooling during solidification allows the melting point of the material to be identified on the time-temperature curve. The melting points can then be plotted versus the composition to give a phase diagram.

### **Experimental Uncertainties**

All the uncertainties were calculated using the law of error propagation, as reported elsewhere.<sup>1</sup> Here, the previously reported results will be briefly summarized.

The total uncertainty of the mass of sample mixture was less than 0.01 g. The uncertainty in composition measurements was estimated to be always lower than 0.005 in mole fraction.

The total uncertainty for the temperature, using the law of error propagation, was calculated to be less than 0.023 K.

Since the measured vapor-pressure data were not accurately measured at very low temperatures within the declared precision of the used instrument (the pressure values were acquired by an absolute pressure transducer HBM, Mod. P8A, and the global uncertainty of the pressure measurements was estimated to be less than 3 kPa), the vapor-pressure data were not reported in the present paper.

### **Experimental results**

*Chemicals.* Carbon dioxide was supplied by Sol SpA. Their purity was checked by gas chromatography, using a thermal conductivity detector, and was found to be 99.99% basing all estimations on an area response. Dimethyl ether was provided by Aldrich Inc., USA. It was

degassed by immersion in liquid nitrogen and evacuation. Its purity was checked by gas chromatography using a thermal conductivity detector and its mass fraction was found to be better than 99.8 % by analysis of peak area.

*Pure fluids.* The triple point temperatures for the mixture constituent fluids were obtained in different experiments, and different runs were repeated for each pure fluid. These data relate to the tests conducted with the stirrer switched on.

For carbon dioxide, the measurements were reported elsewhere [6-7]. For the fluid, a metastable phase was appearing during the measurements. In addition, a faster cooling rate coincided with a greater supercooling effect. The cooling rate that seemed to guarantee the greatest repeatability of the results was approximately  $-0.01$  K/s, corresponding to an air flow rate of approximately  $0.17$  dm<sup>3</sup>/s. Triple-point measurements showed good agreement with literature sources, both in terms of temperature and pressure [6-7].

For dimethyl ether, the metastable phase was not observed during the measurements. A change of slope was evident in the temperature-time diagram during the heating. The triple point measurement ( $T_p=131.58$ ) revealed a very good consistency with the literature value ( $T_p=131.65$  K) [11-12].

*Results for mixtures.* Regarding the studied binary system, no literature data on the SLE are available in the open literature. Measurements were taken using different concentrations of the two components, obtaining a satisfactory number of points, which were then recorded on a concentration/temperature graph ( $T$ - $x$ ).

Conducting several tests on the same sample, we noted that we obtained better, more reliable results by switching off the stirrer at least about 20-40 K (values suggested by experience) before reaching the triple point temperature. This was probably due to the turning of the stirrer, that helps to keep the mixture's components well mixed and the homogeneity of temperature inside the cell, but once near-freezing temperatures have been reached, it probably interferes with the solidification of the mixture, fragmenting the solid crystals when they began to form.

In figure 2 the  $T$ - $x$  measurements for the DME + CO<sub>2</sub> system are reported. The results were also summarized in Table 1.

*Rossini method corrections.* The results of the temperature data acquisitions were corrected using the Rossini method [13] because a constant cooling rate is not indispensable and was not guaranteed by our experimental method. The entity of the corrections takes into account the fact that the fluid is still in a liquid state during the metastable state (supercooling) that precedes proper solidification. In this phase, the temperature is distinctly lower than the one characterizing the instant when crystallization begins, its amplitude depending mainly on the rate at which the temperature is lowered. The resulting corrections were nonetheless always very limited, of the order of a few tenths of a Kelvin in the majority of cases, and always well below 1 K.

### Interpretation of the results

When an organic system forms eutectic, the course of the *liquidus* is well described by the Schröder equation [14]. The SLE depend both on the crystals formed in solution and on the properties of the liquid phase. The exact course of the *liquidus* for mixtures showing a small deviation from Raoult's law depends mainly on the enthalpy of fusion of the solute (CO<sub>2</sub> in our case).

As both systems formed eutectics, the solubility of the solid solute in the solvent (here, DME) can be described by the Schröder equation; which disregarding any difference between the heat capacity of the subcooled liquid solute and solid solute takes the following form:

$$\ln \gamma_2 x_2 = -\frac{\Delta h_m}{RT} \left( 1 - \frac{T}{T_m} \right) \quad (1)$$

where the subscript 2 denotes the solute and the subscript m denotes property at melting point.

Assuming as a first approximation that the solute's activity coefficient,  $\gamma_2=1$ , we can write:

$$\ln x_2 = -\frac{\Delta h_m}{RT} \left( 1 - \frac{T}{T_m} \right) \quad (2)$$



This simplification leads to the consideration that the solubility of the solid solute is independent of the solvent as far as the assumptions hold. The enthalpies at melting point ( $\Delta h_m$ ) were assumed to be  $9020 \text{ J}\cdot\text{mol}^{-1}$ , [15] and  $4937 \text{ J}\cdot\text{mol}^{-1}$ , [16] for  $\text{CO}_2$ , and DME, respectively.

The course of the liquidus calculated with the Schröder equation is included in Figure 2. The system showed a discrepancy quite noticeable with the Schröder equation prediction at lower carbon dioxide concentration (measurements were about 15-20 degrees higher than the predicted values) and of few degrees (about 5-10 degrees lower) at higher carbon dioxide concentration.

## Conclusion

In this paper, the solid-liquid equilibria of dimethyl ether + carbon dioxide system was measured down to temperatures of 131.6 K. The binary system is potentially suitable working fluids in low-temperature refrigeration applications. The triple point of dimethyl ether was measured to check the reliability of the new apparatus, revealing a good consistency with the literature.

The system showed a discrepancy quite noticeable with the Schröder equation prediction.

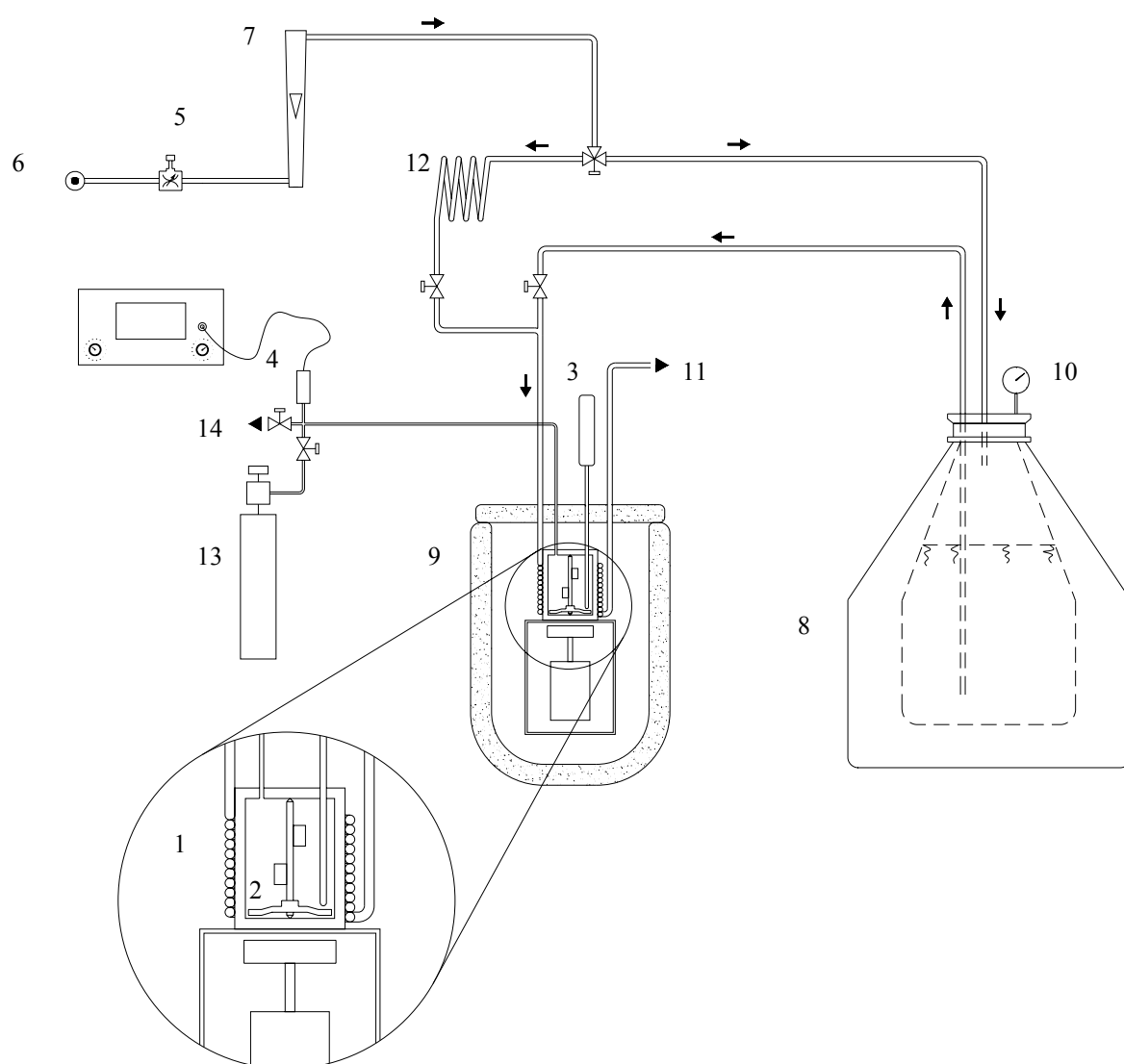
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**Table 1**  $T$ - $x$  Measurements for the CO<sub>2</sub> + DME Binary System

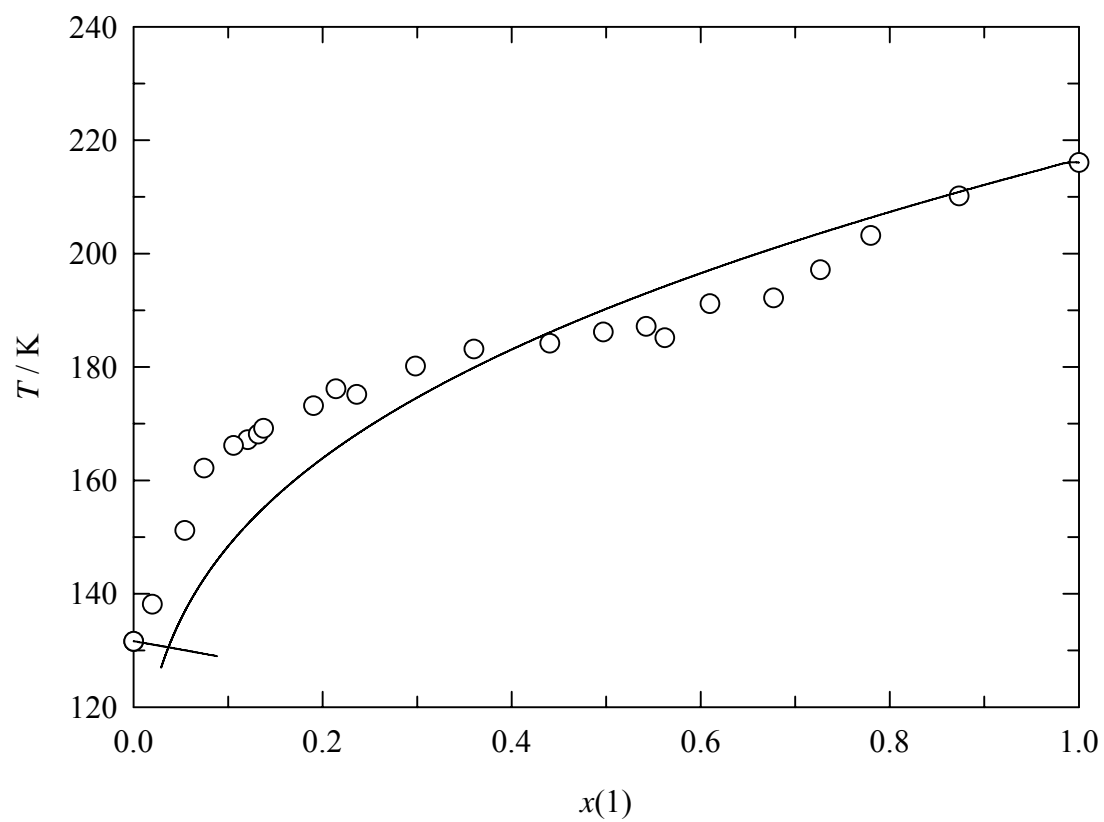
CO <sub>2</sub> (1) + DME (2)	
$x$ (1)	$T$ /K
0.000	131.58
0.000	131.61
0.020	138.15
0.054	151.15
0.074	162.15
0.106	166.15
0.121	167.15
0.132	168.15
0.138	169.15
0.190	173.15
0.214	176.15
0.236	175.15
0.298	180.15
0.360	183.15
0.440	184.15
0.497	186.15
0.542	187.15
0.562	185.15
0.610	191.15
0.677	192.15
0.727	197.15
0.780	203.15
0.873	210.15
1.000	216.05



**Fig 1** Schematic illustration of the apparatus

Notation:

- |    |                                       |
|----|---------------------------------------|
| 1  | Measurement cell                      |
| 2  | Stirrer                               |
| 3  | Platinum resistance thermometer       |
| 4  | Pressure transducer                   |
| 5  | Mass flow controller                  |
| 6  | Dry air supplier                      |
| 7  | Rotameter                             |
| 8  | Liquid nitrogen tank                  |
| 9  | Dewar containing the measurement cell |
| 10 | Liquid nitrogen dewar manometer       |
| 11 | Nitrogen outlet                       |
| 12 | External heating coil                 |
| 13 | Charging bottle                       |
| 14 | Vacuum pump system                    |



**Fig. 2** SLE for the  $\text{CO}_2$  (1) + DME (2) system. The lines denote the Schröder eq.